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(54) [Title of the invention] Method for producing unsaturated carboxylic acid

(57) [Abstract]

[Problem] To obtain target unsaturated carboxylic acid such as acrylic acid or methacrylic acid at a higher space-time yield without any decrease in the selectivity of the target compound, using saturated hydrocarbon such as propane or isobutane as starting material.

[Overcoming means] A method for producing unsaturated carboxylic acid by the gas phase catalytic oxidation of saturated hydrocarbon of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst, where said catalytic reaction is performed at a contact time of no more than 10 s and a reaction pressure of no less than 152 KPa.

[Scope of the patent claims]

[Claim 1] A method for producing unsaturated carboxylic acid by the gas phase catalytic oxidation of saturated hydrocarbon of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst, where said catalytic reaction is performed at a contact time of no more than 10 s and a reaction pressure of no less than 152 KPa.

[Claim 2] A method for producing unsaturated carboxylic acid as claimed in claim 1, where the saturated hydrocarbon of from 3 to 8 carbon atoms is propane and the unsaturated carboxylic acid is acrylic acid.

[Claim 3] A method for producing unsaturated carboxylic acid as claimed in claim 1, where the saturated hydrocarbon of from 3 to 8 carbon atoms is isobutane and the unsaturated carboxylic acid is methacrylic acid.

[Detailed description of the invention]

[0001]

[Technical field of the invention] The present invention relates to a method for producing unsaturated carboxylic acid by the gas phase catalytic oxidation of saturated hydrocarbon of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst. Specifically, it relates to a method for producing acrylic acid from propane, methacrylic acid from isobutane, maleic anhydride from normal butane, and maleic anhydride and phthalic anhydride from pentanes, by the gas phase catalytic oxidation of saturated hydrocarbon such as propane or isobutane in the presence of molecular oxygen and catalyst.

[0002]

[Prior art] Many methods have already been suggested for the production of unsaturated oxygen-containing compounds and/or unsaturated hydrocarbons by the gas phase catalytic oxidation of saturated hydrocarbons of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst. Some are already used industrially, such as the production of maleic anhydride from normal butane, although many are not used industrially. For example, Japanese Unexamined Patent Application Numbers S55-62041, H2-83348, H6-199731, H6-218286, H6-279351 and H7-10801 and the like relate to methods for producing oxygen-containing compounds (acrolein, acrylic acid, etc.) and/or propylene using propane as starting material, and Japanese Unexamined Patent Application Numbers S55-6204, H3-20237, H4-59738, H4-59739, H4-128247, H5-178774, H5-213799, H6-211725, Japanese Examined Patent Publication Numbers H7-33344, H7-116071, H8-5820, H8-32644, and Japanese Patent Number 2558036 and the like relate to methods for producing oxygen-containing compounds (methacrolein, methacrylic acid, etc.) and/or isobutylene from isobutane. The applicants also report Japanese

Unexamined Patent Application Numbers H3-106839, H7-10782, H8-12606, H9-12490 and H9-20700.

[0003]

5 In practice, the saturated hydrocarbon conversion rate, the selectivity and space-time yield (STY: the amount of target compound produced per unit catalyst) of the target oxygen-containing compound, and the lifetime of the catalyst are important factors when unsaturated oxygen-containing compounds and/or unsaturated hydrocarbons are produced using these production methods, but in practice, with the exception of the production of maleic anhydride from normal butane, there has not
10 yet been developed a reaction method which is satisfactory in terms of all of these factors.

[0004]

If we consider conversion rate, it has not been possible to develop a catalyst and reaction method which result in a satisfactory yield of target oxygen-containing
15 compound by a one path reaction alone, as in production methods which use unsaturated hydrocarbon as starting material and in the production of maleic anhydride from normal butane, where the product does not undergo gradual oxidation readily, because the reactivity of the starting material saturated hydrocarbon is extremely poor. In practice, there is nothing for it but to recycle the
20 unreacted saturated hydrocarbon, but this still results in a marked decrease in selectivity due to the gradual oxidation of the target unsaturated oxygen-containing compound and/or unsaturated hydrocarbon when rigorous reaction conditions are imposed, for example, when the reaction temperature is increased, in order to improve selectivity. There is a further disadvantage in that increasing the reaction
25 temperature shortens the catalyst lifetime.

[0005]

One important factor in determining the cost of producing the target compound is the space-time yield. Whatever the high yield catalyst or process employed, if the space-time yield is low, the size of the reactor and the amount of catalyst required to
30 maintain any prescribed level of production will be larger, and supplementary equipment will also be larger and so production costs will rise. Conversely, if the space-time yield is high, production costs will be lower, which is advantageous. Consequently, improving the space-time yield has a considerable effect on production costs in processes which require the recycling of unreacted starting
35 material.

[0006]

Nevertheless, current production technology has very few examples of control by means of the space-time yield concept. As described above, the conversion rate decreases when the reaction is performed at a low temperature in order to achieve

oxidation of these saturated hydrocarbons at good selectivity. There are many examples of increasing the concentration of the starting material saturated hydrocarbon in order to improve the space-time yield for the oxidation of said saturated hydrocarbon. For example, in Japanese Examined Patent Application
5 Numbers H7-116071, H8-5820 and H8-32644, even though the isobutane oxidation reaction is performed using a high isobutane content (60%), the calculated space-time yield is low, 1 mmol/g-cat/h, despite the fact that the reaction temperature was high (the reaction tube was inserted into a constant temperature oven at 340°C or higher). Moreover, the space-time yield was around
10 2 mmol/g-cat/h, even at the upper temperature limit for Keggin-type heteropolyacid catalysts (that is, when the constant temperature oven was at 370°C). In Patent Number 2558036, methacrolein and methacrylic acid are synthesized at high productivity by the same isobutane oxidation, despite the fact that the isobutane concentration is 50% and the reaction temperature is low (280°C). However, as the
15 composite oxide catalyst used contains phosphorus and vanadium, the main product is methacrolein, and in order to obtain methacrylic acid it is necessary to perform a further oxidation step, which is industrially disadvantageous.

[0007]

It is common knowledge that increasing the partial pressure of the reaction starting
20 material will increase the rate of reaction, but although in the prior art there are examples of increasing the starting material concentration, there are no known examples of increasing the reaction pressure in order to increase the partial pressure. The reaction rate of gas phase oxidation is usually increased by increasing the reaction pressure, but it is known that this is disadvantageous because the target
25 products are gradually oxidized and selectivity decreases. Lower reaction pressures are therefore conventionally thought to be desirable. Despite the fact that it is disclosed in the prior art relating to the oxidation of propane and isobutane that increased reaction pressure conditions are possible, the present applicants only know of the disclosure "more preferably 2 atmospheres or less, and around
30 atmospheric pressure is more preferable", and do not know of embodiments which involve the use of reaction pressures of 152 KPa or higher.

[0008]

[Problems to be overcome by the invention] Given this situation, the present inventors aimed to produce unsaturated carboxylic acids such as acrylic acid or
35 methacrylic acid using saturated hydrocarbons such as propane or isobutane as starting material, at high target productivity per unit catalyst without decrease in target product selectivity, that is, they aimed to discover a production method with an excellent space-time yield; as a result of their diligent research, they perfected the

present invention upon discovering that the abovementioned aim is completely satisfied when specific operational conditions are employed.

[0009]

5 [Means of overcoming the problem] Specifically, the present invention provides a method for producing unsaturated carboxylic acid by the gas phase catalytic oxidation of saturated hydrocarbon of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst, where said catalytic reaction is performed at a contact time of no more than 10 s and a reaction pressure of no less than 152 KPa.

[0010]

10 [Mode of the invention] In an embodiment of the present invention, examples of the saturated hydrocarbon of from 3 to 8 carbon atoms which is used as the reaction starting material include propane and isobutane, and these are subjected to gas phase catalytic oxidation in the presence of molecular oxygen and catalyst to yield unsaturated carboxylic acid such as acrylic acid and/or methacrylic acid. In the case
15 of said reaction for producing unsaturated oxygen-containing compound and/or unsaturated hydrocarbon by the gas phase catalytic oxidation of saturated hydrocarbon of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst, the present invention is such that, with various catalysts, the reaction is performed on increasing the reaction pressure to at least 152 KPa while maintaining
20 the optimum contact time under normal pressure reaction conditions, or a value close to that retention time, and so the increase in reaction pressure raises the starting material partial pressure and results in a better space-time yield, with no decrease in the selectivity or in the rate of conversion of the starting material saturated hydrocarbon of from 3 to 8 carbon atoms to the target compound.

25 [0011]

If the catalyst used in the present invention is one which is used conventionally in the production of unsaturated oxygen-containing compounds and/or unsaturated hydrocarbons by the gas phase catalytic oxidation of saturated hydrocarbons of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst, productivity
30 can be improved under the reaction conditions suggested in the present invention regardless of the composition and shape of said catalyst. Specifically, the catalyst may be a heteropolyacid-based catalyst having phosphorus and molybdenum as main components, a composite oxide catalyst having phosphorus and vanadium as main components, a composite oxide catalyst having phosphorus, molybdenum and vanadium as main components, or a heteropolyacid catalyst, a composite oxide catalyst having niobium, molybdenum, vanadium and antimony as main components, a heteropolyacid catalyst having phosphorus, molybdenum, vanadium, antimony and/or arsenic as main components, a phthalium-containing composite oxide catalyst, a composite oxide catalyst having niobium, molybdenum, vanadium
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and tellurium as main components, a composite oxide catalyst having bismuth, vanadium, molybdenum and silver as main components, or the like. Particularly recommended is the use of a catalyst comprising a partially neutralized salt of a Keggin-type heteropolyacid represented by the general formula $P_aMo_bV_cX_dY_eZ_fO_g$ (in the formula, P, Mo, V and O represent phosphorus, molybdenum, vanadium and oxygen, respectively; X represents at least one element chosen from the group consisting of copper, silver, bismuth, iron, cobalt, lanthanum and cerium; Y represents at least one element chosen from the group consisting of alkali metals, alkaline earth metals and phthalium; Z represents arsenic, antimony, bismuth, germanium, cerium or tellurium, and the subscripts a, b, c, d, e, f and g represent the atomic ratios of the various elements, where $b = 12$, a, c and d are values not greater than 3 but not including 0 (zero), d, e and f represent values not greater than 3, including 0, and g represents a value which depends on the atomic ratios and oxidation states of the various elements other than oxygen).

15 [0012]

The achievable reaction pressure depends on the shape and properties of the catalyst used, although it is usually preferable to maintain the optimum contact time under normal pressure or a value close to that retention time. Specifically, by allowing the space velocity (unit/h) (SV: found from the relationship between the amount of reaction starting material supplied under standard conditions (calculated at atmospheric pressure of 25°C) and the amount of catalyst) to increase such that the SV is doubled when the pressure is doubled or trebled when the pressure is trebled, the present invention allows the space-time yield to be doubled or trebled with hardly any variation in the conversion rate or selectivity.

25 [0013]

In a common fixed bed flow type reactor, the pressure at the inlet of the reactor increases to some extent as a result of the loaded catalyst. This pressure increase varies depending on the layer length and shape of the catalyst used and the space velocity of the reaction gas, and the reaction pressure employed in the present invention can be achieved by applying additional pressure to that achieved under the reaction conditions currently employed industrially for gas phase oxidation. Specifically, the pressure is not less than 152 KPa.

[0014]

35 The concentration of the saturated hydrocarbon in the starting material gas supplied to the reaction can be from 1 to 85 mol%, preferably from 3 to 70 mol%. The reaction for producing unsaturated oxygen-containing compounds and/or unsaturated hydrocarbons by the gas phase catalytic oxidation of saturated hydrocarbons in the presence of molecular oxygen and catalyst is industrially advantageous in that the reaction rate is often first order for the concentration of the

saturated hydrocarbon and so in that region, the higher the concentration of saturated hydrocarbon in the starting material gas, the greater the space-time yield.

[0015]

5 The concentration of the molecular oxygen must be decided according to the concentration of the starting material saturated hydrocarbon and on considering that the system must not become explosive at that concentration. It should be noted that air, pure oxygen, oxygen-enriched air or the like can be used as the molecular oxygen.

[0016]

10 In addition to the starting material saturated hydrocarbon and molecular oxygen, the starting material gas applied to the reaction may also contain water vapor, diluent gases, nitrogen, saturated hydrocarbons which have a different structure and/or number of carbon atoms to the starting material, carbon monoxide, carbon dioxide, and unsaturated oxygen-containing compounds and unsaturated hydrocarbon
15 products. The water vapor in particular is not merely present as a diluent for removing the heat of reaction and preventing the system from becoming explosive, as water vapor participates in some reaction systems and catalyst systems, having a favorable effect on conversion rate, selectivity and catalyst lifetime, and in such systems, water vapor is preferably present at up to 30 mol%.

20 [0017]

In the present invention the type of reaction is not limited to a fixed bed type; fluidized bed and transfer bed type reactions and the like can be employed.

[0018]

[Advantages of the invention] The method of the present invention is extremely
25 valuable industrially because when unsaturated carboxylic acid is produced by the gas phase catalytic oxidation of saturated hydrocarbon of from 3 to 8 carbon atoms in the presence of molecular oxygen and catalyst according to said method, it is possible to obtain target unsaturated carboxylic acid at a higher space-time yield without a decrease in target compound selectivity, even when the same catalyst is
30 used, by the extremely simple method of stipulating the reaction pressure and the contact time between the starting material and the catalyst (reaction time).

[0019] [Working examples]

The present invention is described specifically below by means of working examples, although the present invention is not limited to these working examples. It should be
35 noted that in the present invention, the space velocity, contact time, conversion rate, selectivity and space-time yield are defined as follows.

[0020]

Space velocity (l/h) = (starting material gas supply rate (based on standard conditions (ml/h)) ÷ (amount of catalyst (ml)))

Contact time(s) = $60 \times 60 \times (\text{reaction pressure (KPa)} / 100) \div (\text{space velocity (l/h)})$

Conversion rate (%) = $[(\text{number of moles of saturated hydrocarbon reacted}) \div (\text{number of moles of saturated hydrocarbon supplied})] \times 100$

Selectivity (%) = $[(\text{number of moles of unsaturated carboxylic acid produced}) \div (\text{number of moles of saturated hydrocarbon reacted})] \times 100$

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Space-time yield (mmol/ml/h) = $\text{space velocity (l/h)} \times (\text{starting material saturated hydrocarbon supply gas concentration (\%)}) \times (\text{conversion rate (\%)}) \times (\text{selectivity (\%)}) \div 22.4 \div 10^6$

[0021] Working example 1

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21.0 g of 85% orthophosphoric acid, 6.05 g of copper phosphate $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, 38.2 g of cesium nitrate and 13.3 g of 60% aqueous arsenic acid were added to 230 g of ion exchange water and dissolved with agitation to yield a uniform aqueous solution (referred to as solution A). Next, 330 g of ion exchange

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water were loaded into a 1l autoclave, the temperature was maintained at 40°C, then 296.5 g of ammonium molybdate $[(\text{NH}_4)_6\text{MoO}_3 \cdot 4\text{H}_2\text{O}]$ were added and dissolved with agitation. All of solution A was injected into the resulting solution and a precipitate formed to yield a slurry, then 6.36 g of vanadium pentoxide V_2O_5 were added. The internal temperature of the autoclave was raised to 120°C

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and the system was matured for 12 hours, then the water content was evaporated off in a dryer at 120°C to yield dry solid. 4 parts of ceramic fibers and 19 parts of ion exchange water were added to 100 parts of the dry solid catalyst slurry, and the resulting system was milled then extrusion molded to a diameter (ϕ) of 3 mm. The extrusion molding was dried then subjected to salt degradation (removal of ammonium nitrate, removal of nitrate radicals), which was performed by heating to

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250°C under a current of air, then the system was baked for 3 hours at 435°C under a current of nitrogen to yield the catalyst. The composition of this catalyst (excluding oxygen atoms) was $\text{Mo}_{1.2} \text{V}_{0.5} \text{P}_{1.5} \text{As}_{0.4} \text{Cu}_{0.3} \text{Cs}_{1.4}$, and infrared absorption spectroscopy and X-ray diffraction confirmed that it had a cubic Keggin-type heteropolyacid structure. 4 ml of this catalyst was loaded into a 15 mm internal

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diameter glass reaction tube, starting material gas comprising 37 mol% isobutane, 37 mol% oxygen, 16 mol% water vapor, with the remainder being nitrogen, was passed through at a space velocity (based on standard conditions) of 204 l/h, and the reaction pressure was increased to 200 KPa, and its activity was tested at a reaction temperature of 329°C. It should be noted that the contact time was 3.5 s.

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The isobutane conversion rate was 7.1%, the methacrylic acid selectivity was 55.5%. The space-time yield (STY) was 1.33 mmol/ml/h.

[0022] Comparative example 1

Activity was tested by the same method as in working example 1, using the catalyst prepared in working example 1, but the starting material gas was passed through the

reaction tube at a space velocity (based on standard conditions) of 1025/h, and the reaction pressure was normal pressure (100 KPa). It should be noted that the contact time was 3.5 s, and the activity was tested at 330°C, almost the same as the reaction temperature used in working example 1. The isobutane conversion rate was 7.6%, the methacrylic acid selectivity was 57.4% and the space-time yield (STY) was 0.74 mmol/ml/h.

[0023] Working example 2

Activity was tested by the same method as in working example 1, using the catalyst prepared in working example 1, but the starting material gas was passed through the reaction tube at a space velocity (based on standard conditions) of 2744/h, and the reaction pressure was 270 KPa. It should be noted that the contact temperature was 3.5 s, and the activity was tested at 332°C, almost the same as the reaction temperature used in working example 1. The isobutane conversion rate was 9.0%, the methacrylic acid selectivity was 51.9% and the space-time yield (STY) was 2.12 mmol/ml/h.

[0024] Comparative example 2

Activity was tested by the same method as in working example 1, using the catalyst prepared in working example 1, but the starting material gas was passed through the reaction tube at a space velocity of 2059/h, the amount of catalyst used was 0.5 ml, the reaction pressure was normal pressure (100 KPa), and the activity test was performed at a contact time of 1.8 s. It should be noted that at that time the reaction furnace temperature was 354°C in order to maximize the space-time yield (STY). The isobutane conversion rate was 8.3%, the methacrylic acid selectivity was 50.4% and the space-time yield (STY) was 1.41 mmol/ml/h.

[0025] Working example 3

An activity test was performed by the same method as in comparative example 2 using the catalyst prepared in working example 1, except that the starting material gas was passed through the reaction tube at a space velocity (based on standard conditions) of 7605/h and the reaction pressure was 370 KPa. It should be noted that the contact time was 1.8 s and the reaction temperature was similar to that in comparative example 2 in that the reaction for this temperature was 355°C. The isobutane conversion rate was 12.0%, the methacrylic acid selectivity was 43.8% and the space-time yield (STY) was 6.60 mmol/ml/h.